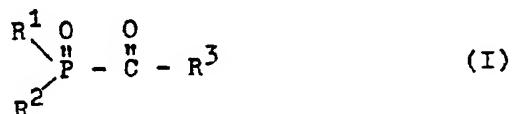


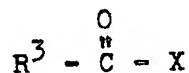
Abstract

Process for the preparation of acylphosphine oxides

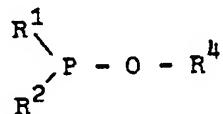
The invention relates to a process for the preparation of acylphosphine oxides. Acylphosphine oxides of the formula



in which R¹ and/or R² are an alkyl radical, cyclohexyl radical, cyclopentyl radical, phenyl radical, a substituted thienyl radical, pyrrolyl radical, pyridyl radical or phenyl radical, or R² is an alkoxy radical, aryloxy radical or arylalkoxy radical, R³ is a tertiary alkyl radical, a tertiary cycloalkyl radical or a thienyl radical, pyrrolyl radical, furyl radical, pyridyl radical, phenyl radical or naphthyl radical which optionally carries halogen groups, alkyl groups, alkylthio groups, alkoxy groups, cycloalkyl groups or phenyl groups, are prepared by reacting an acid halide of the formula



in which X is Cl or Br, with an alkoxyphosphine of the formula



in which R⁴ is an alkyl radical or cycloalkyl radical, at 20 to 150°C, if appropriate in the presence of an inert organic solvent and a tertiary amine. The acylphosphine oxides prepared according to the invention are suitable as photoinitiators.

Process for the preparation of acylphosphine oxides

The invention relates to a process for the preparation of acylphosphine oxides.

5

DE-A 28 30 927 and 29 09 994 already disclose acylphosphine oxides, a process for their preparation and their use as photoinitiators.

10 The preparation process described therein, however, can only be carried out with high yields if freshly distilled acid chloride and alkoxyphosphine are used. Even traces of water in the acid chloride, which are difficult to exclude during implementation on an industrial scale, bring the reaction to a standstill.

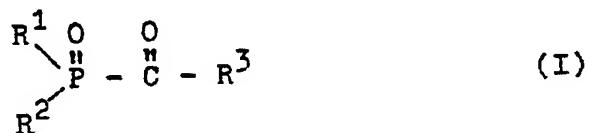
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It is an object of the present invention to propose a process which is more advantageous compared with this.

20 Surprisingly, it has been found that this is possible by adding from 1 to 20 mol% of tertiary amine to the reaction mixture and the reaction can thus be carried out with reproducibly high yields even on a large scale.

25

The present invention provides a process for the preparation of acylphosphine oxides of the general formula I



30 in which

R¹ and R² are identical or different from one another and are a branched or unbranched alkyl radical, having 1 to 6 carbon atoms, a cyclohexyl radical, a cyclopentyl radical, phenyl radical, a thiaryl,

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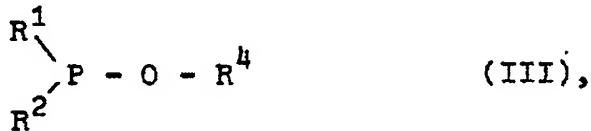
pyrrolyl, pyridyl or phenyl radical substituted by 1 to 3 halogen atoms or by alkyl, alkoxy, alkylthio radicals comprising 1 to 6 carbon atoms, or R² is an alkoxy radical comprising 1 to 6 carbon atoms, an aryloxy radical or an arylalkoxy radical having 1 to 3 carbon atoms in the alkoxy group,

R³ is a tertiary alkyl radical having 4 to 18 carbon atoms, a tertiary cycloalkyl radical having 5 to 18 carbon atoms, a thienyl, pyrrolyl, furyl, pyridyl, phenyl, naphthyl radical or a thienyl, pyrrolyl, furyl, pyridyl, phenyl, naphthyl radical which carries one to four substituents from the group halogen, alkyl, alkylthio, alkoxy radicals comprising 1 to 6 carbon atoms, cycloalkyl radicals or phenyl radicals comprising 5 to 7 carbon atoms,

by reacting an acid halide of the general formula (II)



in which X is Cl or Br, with an approximately equimolar amount of alkoxyphosphine of the general formula (III)

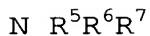


25

in which R⁴ is an alkyl radical comprising 1 to 6 carbon atoms or is a cycloalkyl radical,

at a temperature between 20 and 150°C, if appropriate 30 in the presence of an inert organic solvent.

The process comprises carrying out the reaction in the presence of from 1 to 20 mol%, based on acid halide (II), of a tertiary amine of the general formula (IV)

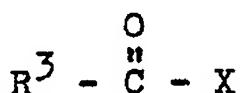


(IV),

in which R^5 , R^6 and R^7 are identical or different from
5 one another and are alkyl radicals comprising 1 to 6
carbon atoms, phenyl radicals or phenyl radicals
substituted by alkyl groups comprising 1 to 3 carbon
atoms.

10 As regards the feed materials and process conditions to
be used for the process according to the invention, the
following is specified.

Suitable acid halides of the general formula (II)



15 are acid chlorides and acid bromides. Preference is
given to the acid chlorides as are specified e.g.
already in DE-A 28 30 927 and 29 09 994. Suitable
alkoxyphosphines of the general formula (III) are
20 likewise those already listed in the aforementioned DE-
As, where R^4 is preferably an alkyl radical comprising
1 to 4 carbon atoms.

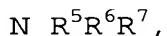
Alkoxyphosphines of this type can be prepared, for
25 example, by the process described by K. Sasse in
Houben-Weyl, Methoden der organischen Chemie [Methods
of organic chemistry], volume 12/1, pages 208 to 209
and 324 to 330, or as described in the German patent
application P 31 01 885.8.

30 The solvents to be used for the process according to
the invention should be inert towards acid chlorides
and phosphines. Solvents of this type are, for example,
ethers, such as dialkyl ethers, e.g. dibutyl ether,
35 diethyl ether, methyl tert-butyl ether, cyclic ethers
such as e.g. dioxane, tetrahydrofuran, aliphatic and

cycloaliphatic hydrocarbons, such as e.g. heptane, cyclohexane; aromatic hydrocarbons such as e.g. benzene, alkylaromatics, such as toluene, xylene, trimethylbenzene, chloroaromatics, such as
5 chlorobenzene, dichlorobenzene; N,N-dialkylamides, such as dimethylformamide or diethylacetamide, dimethylacetamide; chlorinated or fluorinated hydrocarbons such as dichloromethane, 1,1-difluoroethane, 1,2-difluoroethane and mixtures of
10 these solvents. Since chloroform, tetrachloromethane, nitro compounds, sulfoxides and sulfones react with alkoxyphosphines of the formula (III) and compounds carrying primary and secondary amines and also hydroxyl groups react with acid chlorides, they are not suitable
15 as solvents for the process according to the invention.

The inert organic solvents are generally used in amounts of from 0 to 1000, preferably 0 to 300 % by volume, based on the acid chloride.
20

Suitable tertiary amines of the general formula (IV)



25 in which R⁵, R⁶ and R⁷ are identical or different from one another and may be alkyl radicals comprising 1 to 6 carbon atoms, phenyl radicals or phenyl radicals substituted by alkyl groups comprising 1 to 3 carbon atoms, are, for example, trimethylamine, tributylamine,
30 methyldiethylamine, N,N-dipropylaniline and mixtures of these amines; preference is given to triethylamine, tripropylamine, N,N-dimethylaniline and N,N-diethylaniline.
35 Acid chloride (II) and alkoxyphosphine (III) are generally reacted with one another in approximately equimolar amounts.

The tertiary amine is used in amounts of from 1 to 20 mol%, preferably 2 to 10 mol%, based on acid halide (II).

5 A suitable temperature range within which the reaction is carried out according to the invention is a range between about 20 and 150°C, the temperature of the reaction to be chosen within this range also depending on the feed materials. Thus, it is, for example, 10 advisable to choose lower temperatures of about 40 to 80°C when using alkoxyphosphines of the formula (III) where R² = alkoxy radical than when using an alkoxyphosphine where R¹ and R² = phenyl or o-tolyl, for which temperatures between 60 and 110°C are preferred.

15 The application of pressure, for example of 1 to 20 bar, may also be advantageous in order to be able to liquefy alkyl chloride formed during the reaction at temperatures from 20 to 60°C in a technically simple 20 manner.

According to the invention, preferably either the acid chloride (II) and the tertiary amine (IV), without solvent or diluted with a suitable solvent, can be 25 initially introduced and, at temperatures from 20 to 150°C, the alkoxyphosphine (III), undiluted or dissolved in an inert organic solvent, can be added while distilling off the alkylchloride formed, or the alkoxyphosphine (III) is initially introduced together 30 with the tertiary amine (IV), undiluted or dissolved in an inert organic solvent, and the acid chloride (II), undiluted or dissolved in a suitable solvent, is added at a reaction temperature of from 20 to 150°C.

35 The process according to the invention can be particularly advantageously used for the preparation of acylphosphine oxides of the formula (I) in which R¹ and R² have the meaning given above and R³ is an at least disubstituted phenyl radical which is substituted at

the two carbon atoms adjacent to the linkage with the carbonyl group by substituents A and B which are identical or different from one another and are halogen atoms, alkyl, alkylthio or alkoxy radicals comprising 1
5 to 6 carbon atoms, cycloalkyl or phenyl radicals comprising 5 to 7 carbon atoms, or R³ is a 1-naphthyl ring substituted in the 2 and 8 position by A and B or is a 2-naphthyl ring substituted in the 1 and 3 position by A and B.

10

Examples of such compounds which can preferably be prepared according to the invention are given in DE-A 29 09 994 and in the German patent application P 31 33 419.9.

15

If R¹ and R² are phenyl or o-tolyl radicals, the addition of the undiluted, optionally crude (= undistilled) alkoxyphosphine to the undiluted mixture of acid chloride and tertiary amine gives the best
20 yields. For the preparation of compounds of the formula (I) whose melting point is above the reaction temperature, if necessary a suitable inert organic solvent can be added towards the end of the reaction.

25

The addition of the acid chloride (II) to the mixture, diluted if appropriate with inert organic solvents, of alkoxyphosphine (III) and tertiary amine (IV) is particularly advantageous if the more reactive alkyl/aryldialkoxyphosphines of the formula (III) are
30 used. Of inert organic solvent it is possible to co-use here 0 to 10, preferably 0 to 3 parts by volume of solvent/part by weight of alkoxyphosphine.

35

Many of the compounds prepared by the process according to the invention are crystalline and precipitate out of the reaction solution upon cooling and, if appropriate, after drawing off the solvent, or they can be precipitated out from the reaction solution in a suitable manner. Precipitants which can be used here

are alkanes, such as heptane, paraffin or water if the reaction product has been taken up previously in an alcohol such as methanol, ethanol or isopropanol. The resulting products can also be further purified by
5 customary methods.

Liquid acylphosphine oxides obtained according to the invention can be distilled for purification. The tertiary amine present in the reaction solution can, if
10 necessary, be washed out with 5 to 10% strength HCl.

The acylphosphine oxides prepared according to the invention are suitable as photoinitiators.

15 Unless stated otherwise, all of the parts and percentages given in the examples are parts by weight or percentages by weight. Parts by volume are to parts by weight as 1 is to kg.

20 Example 1

Preparation of 2,4,6-trimethylbenzoyldiphenylphosphine oxide

25 For all part examples A, B, C, D, the feed materials trimethylbenzoyl chloride (96% strength, remainder: isomeric acid chlorides) and ethoxydiphenylphosphine (98% strength) were freshly distilled. The concentration of the reaction product 2,4,6-
30 trimethylbenzoyldiphenylphosphine oxide in the reaction solution at the end of the reaction and in the precipitated and dried reaction product was determined using UV spectroscopy (solvent toluene, absorption maximum at 382 nm). The reference used was a sample
35 recrystallized several times, m.p. 92 to 94°C, with an extinction coefficient ϵ (382 nm, toluene) =

656 1.

mol • cm

182.5 parts of 2,4,6-trimethylbenzoyl chloride (II) were initially introduced at 80°C with the additives given in Table 1. Then, with stirring, 235 parts of ethoxydiphenylphosphine (III) (molar ratio 5 (II):(III)=1:1.02) were added dropwise over 90 min and then the mixture was afterstirred for 2 hours at 80°C. The flask contents were weighed, a 0.5 g sample was taken to determine the product content, 220 parts by volume of toluene were added, the mixture was cooled to 10 below 50°C, 185 parts by volume of heptane were added dropwise and the mixture was stirred for 16 hours at room temperature. The mixture was then afterstirred for 2 hours in an ice bath at 0°C, filtered off with suction and dried at 50°C in vacuo. Yield prior to 15 work-up, product content of the dry product and yield in percent of theory are summarized in Table 1.

Table 1: Preparation of 2,4,6-trimethylbenzoyldiphenylphosphine oxide

Experiment	Additives to the trimethylbenzoyl chloride			Yield at the end of the reaction prior to work-up			Yield of isolated product		
	Parts	Triethylamine Mol (based on acid chloride)	H ₂ O	% content in the reaction mixture based on 100% theory		Amount Parts	% content	% theory (based on 100%)	
			Parts	% of theory based on 100%	% of theory based on 100%				
A	0	0	0	77.6	82.5	342.7	87.7	86.4	
B	5	0.05	0	85.4	90.2	330.0	90.1	85.4	
C	0	0	0.36	33.0	36.8	54.3	5.5	0.86	
D	5	0.05	0.36	79.8	85.9	345.0	89.2	88.4	

Experiment A corresponds essentially to Example 1 from DE-A 29 09 994. The addition of 5 parts of triethylamine (experiment B) to the acid chloride does not alter the yield within the margin of error of the 5 UV measurements ($\pm 3\%$). If 2 o/oo of water are added to the initially introduced acid chloride, then the product yield drops to below 50% of the value of A, B. Instead of the desired product, during the work-up corresponding to experiment A, B, another product is 10 isolated which comprises only 5.5% of the desired reaction product. By contrast, the addition of 2 o/oo of water to the amine-containing mixture B (experiment D) does not influence the yield.

15 Example 2

Preparation of 2,4,6-trimethylbenzoylbis(o-tolyl)phosphine oxide

20 2,4,6-Trimethylbenzoyl chloride and methoxybis(o-tolyl)phosphine were firstly freshly distilled.

400 parts of 2,4,6-trimethylbenzoyl chloride (II) were initially introduced into a reaction vessel with the 25 additives given in Table 2 at 100°C. At this temperature, 560.3 parts of methoxybis(o-tolyl)phosphine were added dropwise over the course of 2 hours. The mixture was then stirred for a further 2 hours at 100°C, 220 parts by volume of dioxane were 30 added and the mixture was further stirred for a further hour at 100°C. The mixture was then cooled to 10°C, stirred for 45 minutes at 10°C and the product was filtered off with suction and dried at 80°C in vacuo. The product content of the dry crude product was 35 determined using UV spectroscopy (cf. Example 1) and is summarized together with the yield in percent of theory in Table 2.

Table 2: Preparation of 2,4,6-trimethylbenzoylbis(tolyl)phosphine oxide

	Additives to the trimethylbenzoyl chloride			Yield of isolated product		
	Diethylaniline Parts	Mol based on acid chloride	H ₂ O Parts	Amount Parts	% content	% of theory
A	10	0	0	644.2	98.3	76.6
B	16.4	0.05	0	648.7	97.6	76.5
C	0	0	0.800	72.3	9.2	0.8
D	16.4	0.05	0.800	655.3	95.7	75.8

5 Example 3

Preparation of 2,4,6-trimethylbenzoylphenylphosphinic acid ethyl ester

10 2,4,6-Trimethylbenzoyl chloride and phenyldiethoxyphosphine were firstly freshly distilled.

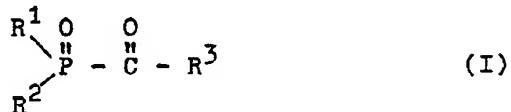
99 parts of phenyldiethoxyphosphine and the additives given in Table 3 were dissolved in 250 parts by volume 15 of toluene. At 80°C, 91.3 parts of 2,4,6-trimethylbenzoyl chloride were added dropwise over 1.5 hours. The mixture was afterstirred for 2 hours at 80°C. Washing was then carried out twice using 35 parts by volume of a 5% strength hydrochloric acid solution 20 which had been saturated at 20°C with sodium chloride, and then washing was carried out with 35 parts by volume of 10% strength aqueous sodium carbonate solution. After stripping off the solvent, a liquid residue remained, the product content of which was 25 determined using UV spectroscopy. The product content of the residue and the yield in % of theory is summarized in Table 3.

Table 3: Preparation of 2,4,6-trimethylbenzoylphenylphosphinic acid ethyl ester

	Additives to the trimethylbenzoyl chloride			Yield of product		
	Triethylamine Parts	Mol based on acid chloride	H ₂ O	Amount	%	% of
				of residue	content	theory
A	0	0	0	158	89.0	89
B	2.5	0.05	0	150	92.3	87.6
C	0	0	0.200	140	27.5	24.4
D	2.5	0.05	0.200	165	83.0	86.7

Claims

1. A process for the preparation of acylphosphine oxides of the general formula I



5

in which

R¹ and R² are identical or different from one another and are a branched or unbranched
10 alkyl radical having 1 to 6 carbon atoms, a cyclohexyl radical, cyclopentyl radical, phenyl radical, a thienyl, pyrrolyl, pyridyl or phenyl radical substituted by 1 to 3 halogen atoms or by alkyl, alkoxy, alkylthio
15 radicals comprising 1 to 6 carbon atoms, or R² is an alkoxy radical comprising 1 to 6 carbon atoms, an aryloxy radical or an arylalkoxy radical having 1 to 3 carbon atoms in the alkoxy group,

20

R³ is a tertiary alkyl radical having 4 to 18 carbon atoms, a tertiary cycloalkyl radical having 5 to 18 carbon atoms, a thienyl, pyrrolyl, furyl, pyridyl, phenyl, naphthyl
25 radical or a thienyl, pyrrolyl, furyl, pyridyl, phenyl, naphthyl radical which carries one to four substituents from the group halogen, alkyl, alkylthio, alkoxy radicals comprising 1 to 6 carbon atoms, cycloalkyl radicals or phenyl radicals comprising 5 to 7 carbon atoms,

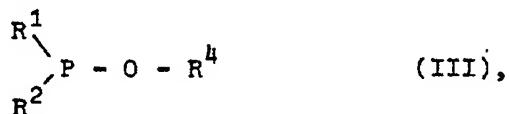
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by reacting an acid halide of the general formula
(II)

35



5 in which X is Cl or Br, with an approximately equimolar amount of alkoxyphosphine of the general formula (III)



10 in which R⁴ is an alkyl radical comprising 1 to 6 carbon atoms, a cyclopentyl radical or cyclohexyl radical,

15 at a temperature between 20 and 150°C, if appropriate in the presence of an inert organic solvent, which comprises carrying out the reaction in the presence of from 1 to 20 mol%, based on acid halide (II), of a tertiary amine of the general formula (IV)



20 in which R⁵, R⁶ and R⁷ are identical or different from one another and are alkyl radicals comprising 1 to 6 carbon atoms, phenyl radicals or phenyl radicals substituted by alkyl groups comprising 1 to 3 carbon atoms.

25 2. The process according to claim 1, wherein the acid chloride and the tertiary amine are initially introduced without solvent or diluted with an inert solvent at 20 to 150°C and the alkoxyphosphine, undiluted or dissolved in an inert solvent, is added while distilling off the alkyl chloride formed at a reaction temperature of from 20 to 150°C.

3. The process according to claim 1, wherein the alkoxyphosphine and the tertiary amine, undiluted or in an inert solvent, are initially introduced and the acid chloride, undiluted or dissolved in an inert solvent, is added at a reaction temperature of from 20 to 150°C.

5

4. The process according to any one of the preceding claims, wherein R³ is an at least disubstituted phenyl radical which is substituted on the two carbon atoms adjacent to the linkage with the carbonyl group by substituents A and B which are identical or different from one another and are halogen atoms, alkyl, alkylthio or alkoxy radicals

10

15 comprising 1 to 6 carbon atoms, cycloalkyl or phenyl radicals comprising 5 to 7 carbon atoms, or R³ is a 1-naphthyl ring substituted in the 2 and 8 position by A and B or a 2-naphthyl ring substituted in the 1 and 3 position by A and B.